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(54) Title: GREASES

(57) Abstract

A grease primarily for use with constant velocity joints comprises a base oil, which may be a mineral oil, or synthetic oil, or a mixture of such oils, and a lithium-based soap thickener, which may be a simple lithium soap or a complex lithium soap, in combination with: (1) an organo-molybdenum complex capable of functioning as a friction reducing additive; (2) an anti-wear/anti-oxidant compound; (3) an organo-sulphur compound extreme pressure additive; and (4) an organo-phosphorus compound extreme pressure additive. A grease in accordance with this formulation has been found to exhibit an unexpected combination of low friction and low wear characteristics when used in constant velocity joints.

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Title: "Greases"

This invention relates to greases intended primarily but not exclusively for use in constant velocity joints.

Greases consist essentially of a base oil with a thickening agent and other additives may be included to promote specific properties, for example extreme pressure lubricants and anti-oxidants.

Whilst the object of such greases is to provide low friction between moving components, in practice the achievement of low friction does not necessary lead to low wear since friction is only one factor which influences wear. In particular, wear may arise as a result of chemical interaction between one or more constituents of the grease and the materials from which the lubricated components are made.

The thickening agent employed is traditionally a soap, but greases formulated in this way cannot achieve the high performance as required by modern technological demands and more recently greases have been made using organic polymers as a thickening agent, particularly polyureas. However, such greases offer little advantage since whilst achieving lower friction, they promote greater wear than traditional soap greases.

The object of the invention is to provide an improved grease offering low friction and low wear which is suitable for use in a constant velocity joint, but may also have other applications, and we have discovered that this can be achieved by utilising a lithium-based soap thickener in combination with other specific materials.

According to the invention we provide a grease comprising a base oil and a lithium-based soap thickener in combination with:-

(1) an organo-molybdenum complex capable of functioning as a friction reducing additive;

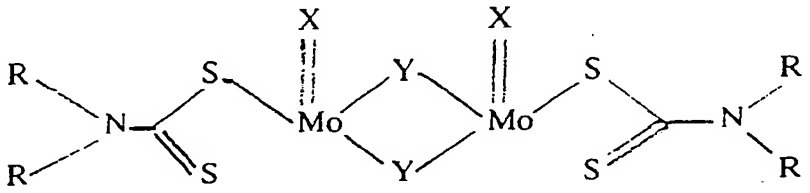
(2) an anti-wear/anti-oxidant compound;

(3) an organo-sulphur compound extreme pressure additive; and

(4) an organo-phosphorus compound extreme pressure additive.

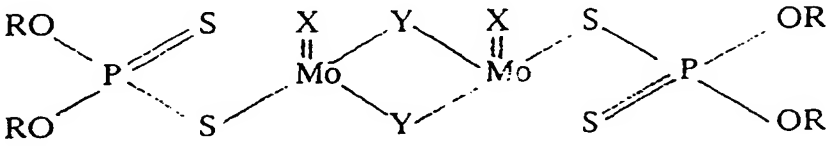
We have shown that greases according to such a formulation may be used as a base grease, together with other conventional additives, such as molybdenum disulphide, in the preparation of a grease composition which in testing and when used in a constant velocity joint provides both low friction and low wear in a manner not achievable by other known grease formulations or other trial formulations differing from the above formulation. It is thought that this combination of properties arises from a synergistic effect obtained by the use of the combination of the organo-sulphur and organo-phosphorus compounds in conjunction with the organo-molybdenum complex and the lithium-based soap.

The organo-molybdenum complex may comprise a molybdenum di-thiocarbamate in accordance with the formula



(I)

or a molybdenum di-thiophosphate according to the formula



(II)

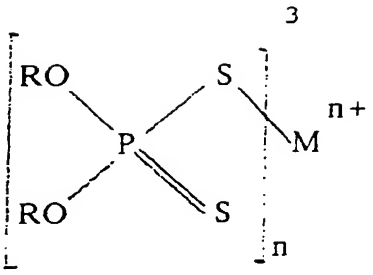
wherein in both cases

X or Y = S or O

R = primary or secondary alkyl or aryl or alkyl substituted aryl group

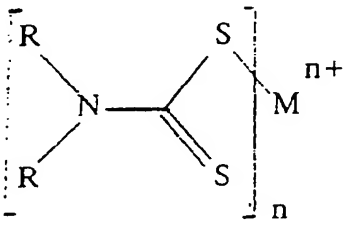
or a mixture of such compounds.

The anti-wear/anti-oxidant compound may comprise an organo-metallic compound such as a metallic di-thiophosphate according to the formula



(III)

or a metallic di-thiocarbamate according to the formula



(IV)

wherein in both cases:-

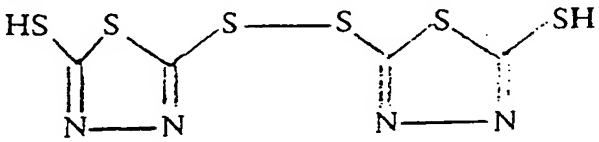
M = Bi, Pb, Sb, Zn, Ni, W or Cd;

R = primary or secondary alkyl or aryl or aryl with an alkyl substituent on the aromatic ring.

or a mixture of such compounds. However, it is envisaged that other types of anti-wear/anti-oxidant compound could be employed.

The organo-sulphur compound may comprise one or more of the following

(a) a substituted 1-thia-3,4-diazole such as 2,5-dithiol-1-thia-3,4-diazole or a sulphur-bridged dimer such as:-



(V)

(b) a synthetic sulphurised sperm oil typically comprising a mixture of unsaturated C_{16} - C_{24} fatty acids and their esters and glycerides which have been sulphurised;

(c) a sulphurised lard;

(d) a sulphurised fatty acid ester;

(e) a sulphurised olefin ester;

(f) a sulphurised spermaceti; or

(g) a tertiary-nonyl sulphide.

The organo-phosphorus compound may comprise one or more of the following:-

(a) a phosphate according to the formula:-

$$[OR]_3P=O \qquad \text{(VI)}$$

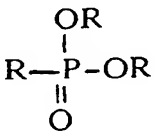
wherein R = alkyl, aryl or alkyl substituted aryl group

(b) a phosphine according to the formula:-

$$[R]_3P=O \qquad \text{(VII)}$$

wherein R = alkyl, aryl or alkyl substituted aryl group

(c) a phosphonate according to the formula:-



(VIII)

wherein R = alkyl, aryl or alkyl substituted aryl group

and

(d) a phosphite according to the formula:-

$$[RO]_3P \qquad \text{(IX)}$$

wherein R = alkyl, aryl or alkyl substituted aryl group

The thickener may comprise a simple lithium soap formed from stearic acid or from 12-hydroxystearic acid or from other similar fatty acids, or a lithium complex soap formed from a mixture of such acids. More particularly, the lithium complex soap may comprise a mixture of hydroxy fatty acids and di-acid salts, such as lithium 12-hyroxystearate and lithium azelate.

Simple lithium soaps and complex lithium soaps when used in formulations in accordance with the invention appear to behave in substantially the same way, except that where the simple soap is employed the grease will operate only up to temperatures of about 120°C, whereas the complex soaps enable temperatures of up to about 180°C to be sustained.

The base oil may comprise a mineral oil or a synthetic oil or a mixture of such oils.

The invention also resides in a method of lubricating a constant velocity joint characterised by the use of such a grease, and further in a constant velocity joint packed with such a grease.

The invention will now be described by reference to the following Examples which illustrate various grease formulations comprising lithium-based thickeners, some of which are in accordance with the invention and others for the purposes of comparison.

In Examples 1 to 10 the base grease comprised a polyalphaolefin containing 10% lithium complex soap thickener consisting of a 60:40 mixture of 12-hydroxystearate and azelate, with the addition of conventional additives such as tackiness agents, corrosion inhibiters and viscosity index improvers.

EXAMPLE 1

A lithium soap grease in accordance with the invention was made by using the above-mentioned base grease and adding thereto:-

2% of an organo-molybdenum complex comprising 2-ethylhexyl-molybdenum di-thiophosphate.

2% of an organometallic anti-wear/anti-oxidant comprising a zinc secondary alkyl di-thiophosphate.

2% of an organo-sulphur compound comprising sulphurised synthetic sperm oil.

1% of an organo-phosphorus compound comprising tritolylphosphate.

EXAMPLE 2

A comparative lithium soap grease not in accordance with the invention was made by using the above-mentioned lithium complex base grease and adding thereto:-

5% of an organo-molybdenum complex comprising 2-ethylhexyl molybdenum di-thiophosphate.

2% of an organo-metallic anti-wear/anti-oxidant comprising antimony di-amyldithiocarbamate.

2% of an organo-sulphur compound comprising a sulphurised fatty acid and ester.

(but no organo-phosphorus compound)

EXAMPLE 3

A further comparison lithium soap grease not in accordance with the invention was made up using the same lithium complex base grease and adding thereto:-

4% of an organo-molybdenum complex comprising 2-ethylhexyl molybdenum di-thiocarbamate.

2% of an organo-metallic anti-wear/anti-oxidant comprising a primary alkyl zinc di-thiophosphate (C=5 to 10)

(but no organo-sulphur or organo-phosphorus compound).

These three greases were tested in an Optimol SRV reciprocating sliding friction and wear machine and compared with a typical calcium complex, low cost, low performance grease (A) and a typical polyurea, low friction, high wear, grease (B) and the results are illustrated in Figure 1 which shows the co-

efficient of friction as measured over a period of one hour at 80°C with a 1.5 mm stroke at 40 Hz and a moderate 200 N load.

Wear in the SRV test was determined by microscopic inspection to obtain a measurement of scar diameter, and a Rank Taylor Hobson Surtronic surface finish measuring machine was employed to determine the depth and cross-section of any scarring. These two measurements were used to calculate wear rate. The term "low wear" as used herein generally indicates that no scar depth was measurable.

As can be seen, the grease of Example 3 performed only a little better in terms of co-efficient of friction than prior art grease (A) and not as well as prior art grease (B) and it also did not exhibit the required low wear characteristic. The grease of Example 2 performed somewhat better than prior grease (B) but again did not exhibit the required low wear characteristics. By contrast the grease in accordance with Example 1, i.e. in accordance with the invention, not only had an improved co-efficient of friction relative to the other greases tested, but also exhibited low wear characteristics, as illustrated in Figure 2 which shows the surface profile of test samples from the SRV tests using the grease of Examples 1 and 2 at moderate load. As can be seen the grease of Example 1 in accordance with the invention shows no significant scarring, whereas that of Example 2 shows some scarring.

Three of these greases where compared with a further prior art low friction clay grease (C) in a test similar to that described above and the results are illustrated in Figure 3 which shows the co-efficient to friction as measured over a period of 30 minutes at 50°C with a 3 mm stroke at 30 Hz and a light 80N load.

Again, only the grease of Example 1, in accordance with the invention, gave a suitably low co-efficient of friction in combination with low wear characteristics.

EXAMPLE 4

A further lithium soap grease in accordance with the invention was made up using the above-mentioned lithium complex base grease and adding thereto:-

5% of an organo-molybdenum complex comprising 2-ethyl hexyl molybdenum di-thiocarbamate.

2% of an organo-metallic anti-wear/anti-oxidant comprising a zinc secondary alkyl di-thiophosphate.

2% of an organo-sulphur compound comprising sulphurised synthetic sperm oil.

2% of an organo-phosphorus compound comprising tritolylphosphate and with the further addition of 5% superfine molybdenum disulphide.

EXAMPLE 5

A further comparative lithium soap grease not in accordance with the invention was made up as in Example 4 but omitting the tritolylphosphate and substituting half of the stated organo-molybdenum complex by a primary alkyl molybdenum di-thiocarbamate.

EXAMPLE 6

A further comparative lithium soap grease not in accordance with the invention was made up as in Example 4 but omitting the tritolylphosphate.

These three greases where compared in a SRV test similar to that described above and following which the wear was determined in the same manner. The friction results are illustrated in Figure 4 which shows the co-efficient of friction as measured over a period of 1 hr at 80°C. with a 3 mm stroke at 40 Hz and a heavy 500 N load.

As can be seen, the greases of Examples 4 and 6 performed significantly better in terms of co-efficient of friction than the grease of Example 5, but only the grease of Example 4 had the required low wear characteristics, as illustrated in Figure 5 which shows the surface profile of test Samples from the SRV tests using greases of Examples 4 and 6 at high load. As can be seen the

grease of Example 6, which is not in accordance with the invention, shows very significant scarring whereas that of Example 4 shows much less scarring.

EXAMPLE 7

A still further lithium soap grease in accordance with the invention was prepared as in Example 1 but using a sulphurised fatty acid ester instead of the sulphurised synthetic sperm oil. Another blend also substituted tri-xylenylphosphate for the tritolylphosphate, giving similar results.

EXAMPLE 8

A still further comparative lithium soap grease not in accordance with the invention was prepared as in Example 2 but replacing half of the stated molybdenum di-thiophosphate by 2-ethylhexyl molybdenum di-thiocarbamate.

EXAMPLE 9

A still further comparative lithium soap grease not in accordance with the invention was prepared using the above-mentioned lithium complex base grease and adding thereto:-

4% of an organo-molybdenum complex comprising an equal mixture of 2-ethylhexyl molybdenum di-thiocarbamate and a primary alkyl molybdenum di-thiocarbamate.

2% of an organo-metallic anti-wear/anti-oxidant comprising a primary alkyl zinc di-thiophosphate (C=5 to 10).

2% of an organo-sulphur compound comprising sulphurised synthetic sperm oil

(no organo-phosphorus compound).

EXAMPLE 10

A still further comparative lithium soap grease not in accordance with the invention was prepared using the above-mentioned lithium complex base grease and adding thereto:-

2% of an organo-metallic anti-wear/anti-oxidant comprising a primary alkyl zinc di-thiophosphate (C=5 to 10).

3% of an organo-sulphur compound comprising sulphurised synthetic sperm oil

(but no organo-molybdenum complex and no organo-phosphorus compound)

These four greases were compared in a further SRV test similar to that described above and again the wear was determined in the same manner. The friction results are illustrated in Figure 6 which shows the co-efficient of friction as measured over 1 hr at 80°C. with a 3 mm stroke at 40 Hz and a moderate 200 N load.

The greases of Examples 8, 9 and 10 all performed similarly with regard to co-efficient of friction at only a moderate value, and only that of Example 10 exhibited the required low wear characteristics, but this grease was not considered to provide a sufficiently low co-efficient of friction. However, the grease of Example 7, in accordance with the invention, showed not only a suitably low co-efficient of friction, but also the required low wear characteristic.

In Examples 11 and 12 which follow, the base grease comprises a mixture of polybutene and mineral oil containing the lithium-based complex soap thickener, also with the addition of conventional additives as previously mentioned.

EXAMPLE 11

A grease in accordance with the invention was made using the last-mentioned base grease and adding thereto:

4% of an organo-molybdenum complex comprising 2-ethylhexyl molybdenum di-thiophosphate

2% of an organo-metallic anti-wear/anti-oxidant comprising a zinc secondary alkyl di-thiophosphate,

2% of an organo-sulphur compound comprising a sulphurised fatty acid ester,

2% of an organo-phospherus compound comprising tri-xylenyl phosphate..

EXAMPLE 12

A further grease, also in accordance with the invention was made in accordance with Example 11 but with the amounts of the specified additives reduced by 50% whilst retaining the same ratio to one another.

These two greases were tested in the same manner as the greases of Examples 1 to 3 and 7 to 10 and the friction results are included in Figures 1 and 4 for ease of comparison with the earlier examples.

As can be seen, results for Example 11 showed slightly higher friction than for Examples 1 and 12 but less than those for Example 2, whereas the results for Example 12 are virtually indistinguishable from those for Examples 1 and 7.

In the case of both these greases, no wear was detected at the end of the SRV test.

Practical testing of these greases has confirmed the superiority of formulations in accordance with the invention relative to both prior art formulations and also various comparative formulations as described above which do not fall within the invention as claimed. Thus in a series of road tests a subjective assessment of noise, vibration and harshness (NVH rating) was carried out using vehicles fitted with constant velocity joints packed with such greases. Additionally laboratory tests were carried out on joints packed with greases in order to determine the life-time of the joint under typical conditions.

The results of such tests are illustrated in Figure 7 which plots the subjective NVH rating against joint life-time. As can be seen prior art grease A had a high (poor) NVH rating but a life-time of greater than 150,000 kilometres (duration of test) whereas prior art grease B achieved an improved NVH rating but failed to survive a 100,000 kilometre test. The grease according to Example 2 (not in accordance with the invention) achieved an NVH rating similar to grease B but only just survived a 100,000 kilometre test, showing signs of serious wear and accordingly not meeting the life-time achieved by grease A.

By contrast greases according to Examples 1 and 7 in accordance with the invention, not only achieved NVH ratings somewhat better than grease B, but also survived 160,000 kilometre life-time tests.

CLAIMS:

1. A grease comprising a base oil and a lithium-based soap thickener in combination with:-

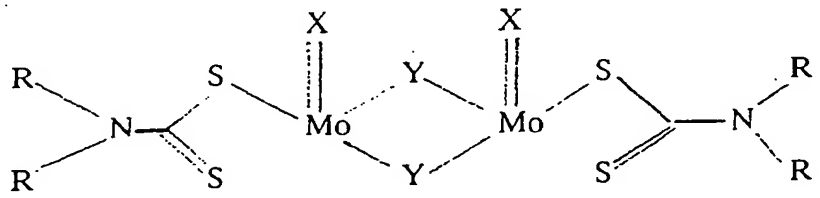
(1) an organo-molybdenum complex capable of functioning as a friction reducing additive;

(2) an anti-wear/anti-oxidant compound;

(3) an organo-sulphur compound extreme pressure additive; and

(4) an organo-phosphorus compound extreme pressure additive.

2. A grease according to Claim 1 wherein the organo-molybdenum complex comprises a molybdenum di-thiocarbamate in accordance with the formula:

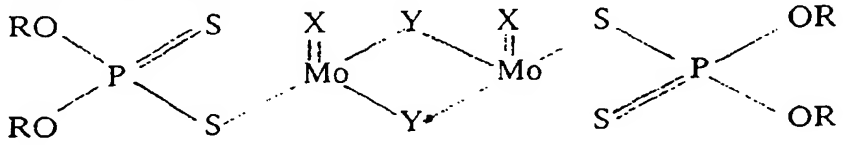


(I)

wherein:

X or Y	=	S or O
R	=	primary or secondary alkyl or aryl or alkyl substituted aryl group.

3. A grease according to Claim 1 wherein the organo-molybdenum complex comprises a molybdenum di-thiophosphate according to the formula:



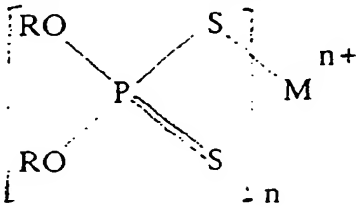
(II)

wherein

X or Y = S or O

R = primary or secondary alkyl or aryl or alkyl substituted aryl group.

4. A grease according to Claim 1 wherein the anti-wear/anti-oxidant compound comprises a metallic di-thiophosphate according to the formula:



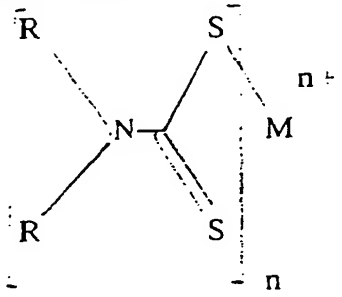
(III)

wherein:

M = Bi, Pb, Sb, Zn, Ni, W or Cd;

R = primary or secondary alkyl or aryl or aryl with an alkyl substituent on the aromatic ring.

5. A grease according to Claim 1 wherein the anti-wear/anti-oxidant compound comprises a metallic di-thiocaramate according to the formula:



(IV)

wherein:

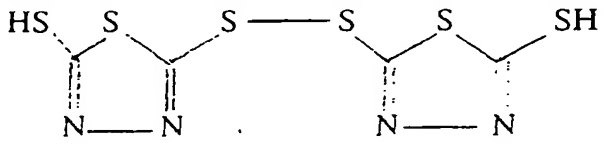
M = Bi, Pb, Sb, Zn, Ni, W or Cd;

R = primary or secondary alkyl or aryl or aryl with an alkyl substituent on the aromatic ring.

6. A grease according to Claim 1 wherein the organo-sulphur compound comprises a substituted 1-thia-3,4-diazole.

7. A grease according to Claim 6 wherein the organo-sulphur compound comprises 2,5-dithiol-1-thia-3,4-diazole.

8. A grease according to Claim 1 wherein the organo-sulphur compound comprises a sulphur-bridged dimer according to the formula:



(V)

9. A grease according to Claim 1 wherein the organo-sulphur compound comprises a synthetic sulphurised sperm oil

10. A grease according to Claim 9 wherein the synthetic sulphurised sperm oil comprises a mixture of unsaturated C_{16} - C_{24} fatty acids and their esters and glycerides which have been sulphurised.

11. A grease according to Claim 1 wherein the organo-sulphur compound comprises a sulphurised lard.

12. A grease according to Claim 1 wherein the organo-sulphur compound comprises a sulphurised fatty acid ester.

13. A grease according to Claim 1 wherein the organo-sulphur compound comprises a sulphurised olefin ester.

14. A grease according to Claim 1 wherein the organo-sulphur compound comprises a sulphurised spermaceti.

15. A grease according to Claim 1 wherein the organo-sulphur compound comprises a tertiary-nonyl sulphide.

16. A grease according to Claim 1 wherein the organo-phosphorus compound comprises a phosphate according to the formula:

$$[OR]_3P=O \qquad (VI)$$

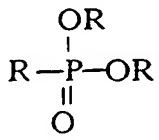
wherein R = alkyl, aryl or alkyl substituted aryl group.

17. A grease according to Claim 1 wherein the organic-phosphorus compound comprises a phosphine according to the formula:

$$[R]_3P=O \qquad (VII)$$

wherein R = alkyl, aryl or alkyl substituted aryl group.

18. A grease according to Claim 1 wherein the organic-phosphorus compound comprises a phosphonate according to the formula:



(VIII)

wherein R = alkyl, aryl or alkyl substituted aryl group.

19. A grease according to Claim 1 wherein the organic-phosphorus compound comprises a phosphite according to the formula:

$$[RO]_3P \qquad (IX)$$

wherein R = alkyl, aryl or alkyl substituted aryl group.

20. A grease according to Claim 1 wherein the thickener comprises a simple lithium soap.

21. A grease according to Claim 20 wherein the lithium soap is derived from stearic acid.

22. A grease according to Claim 20 wherein the lithium soap is formed from 12-hydroxystearic acid.

23. A grease according to Claim 1 wherein the thickener comprises a complex lithium soap.

24. A grease according to Claim 23 wherein the complex lithium soap comprises a mixture of hydroxy fatty acid and di-acid salts.

25. A grease according to Claim 24 wherein the complex lithium soap comprises a mixzture of lithium 12-hydroxystearate and lithium azelate.

26. A grease according to Claim 1 wherein the base oil comprises a mineral oil.

27. A grease according to Claim 1 wherein the base oil comprises a synthetic oil.

28. A method of lubricating a constant velocity joint characterised by the use of a grease in accordance with any one of the preceding claims.

29. A constant velocity joint packed with a grease in accordance with any one of Claims 1 to 27.

30. A grease according to Claim 1 and substantially as hereinbefore described with reference to Example 1.

31. A grease according to Claim 1 and substantially as hereinbefore described with reference to Example 4.

32. A grease according to Claim 1 and substantially as hereinbefore described with reference to Example 7.

33. A grease according to Claim 1 and substantially as hereinbefore described with reference to Example 11.

34. A grease according to Claim 1 and substantially as hereinbefore described with reference to Example 12.

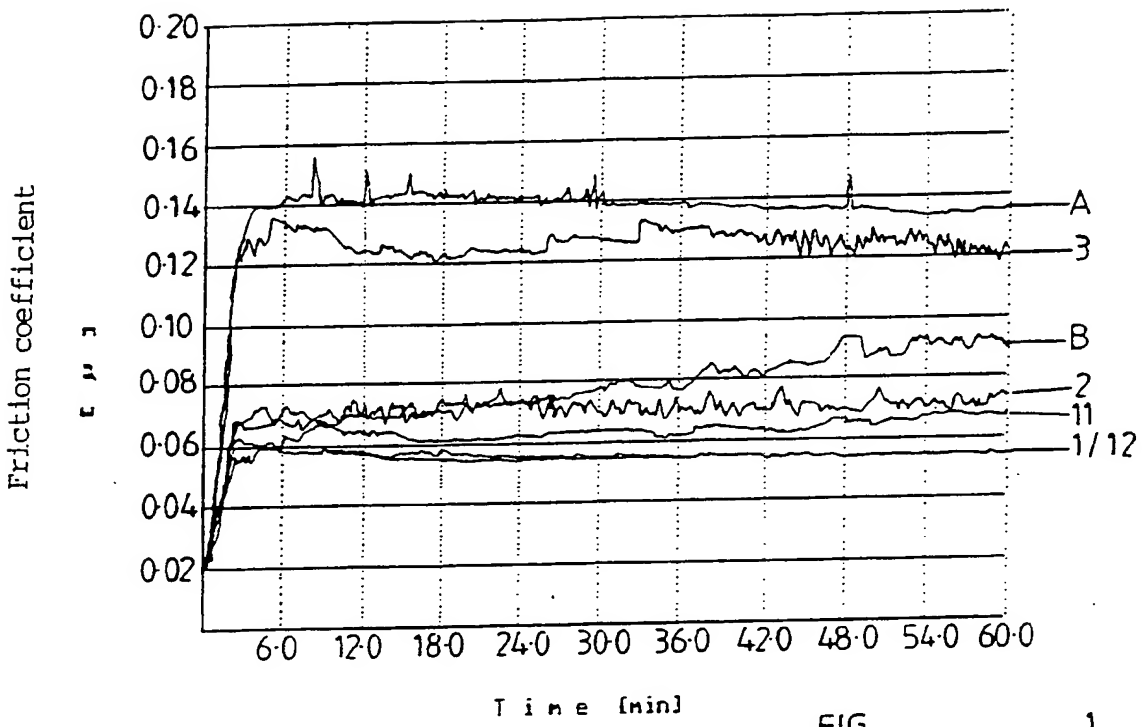

Friction coefficient
0·20
0·18
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
6·0
12·0
18·0
24·0
30·0
36·0
42·0
48·0
54·0
60·0
Time [min]
A
3
B
2
11
1/12

FIG 1

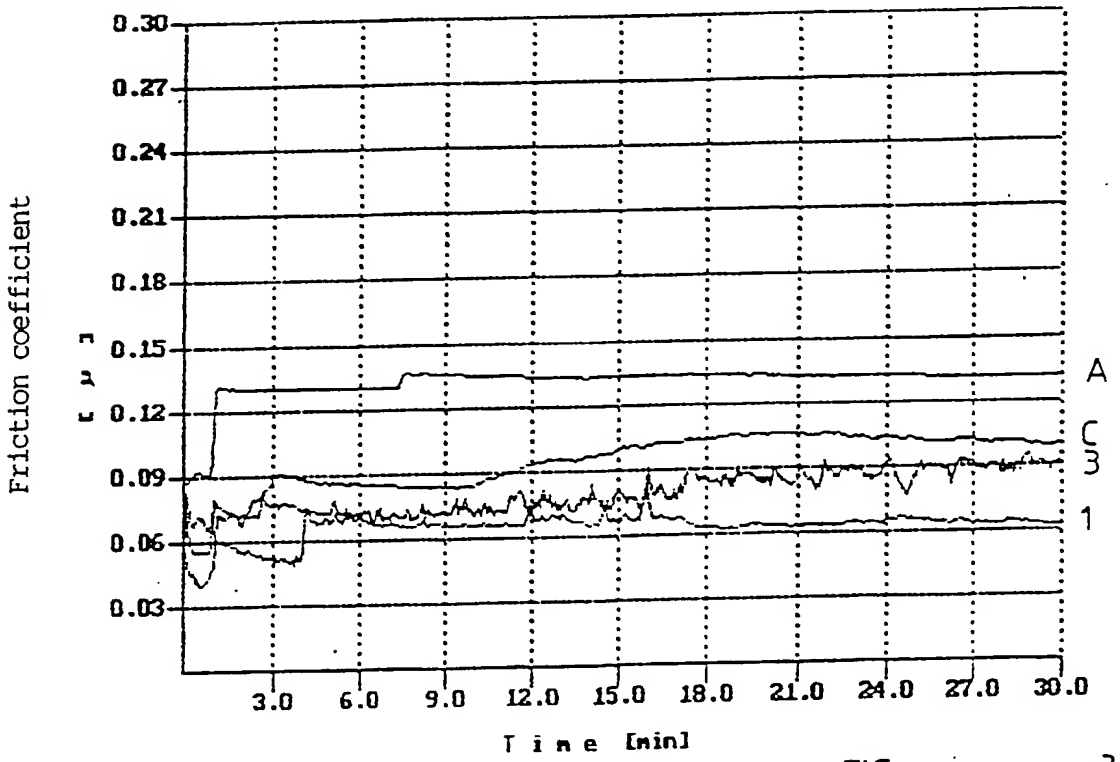
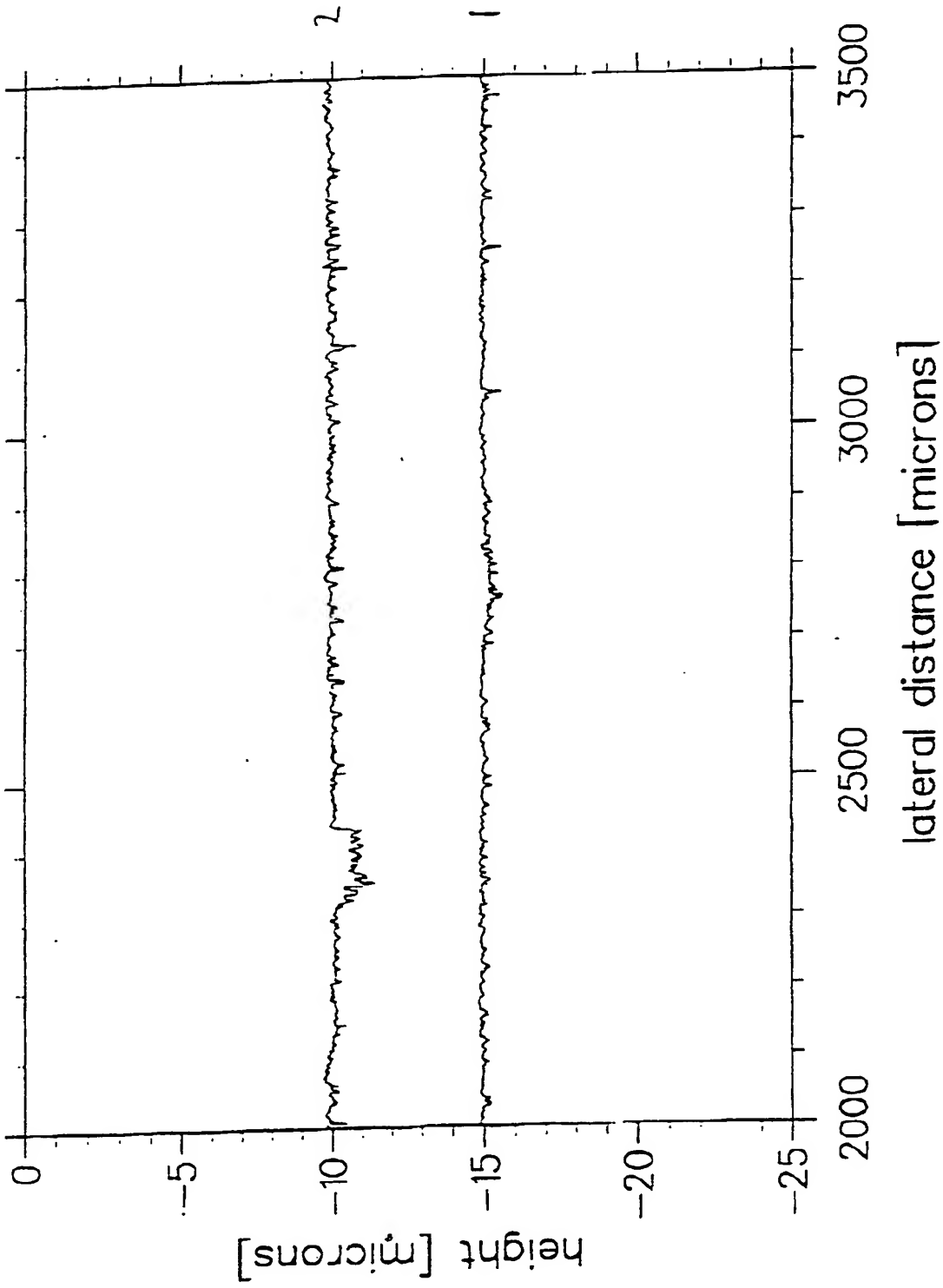

Friction coefficient
0.30
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
3.0
6.0
9.0
12.0
15.0
18.0
21.0
24.0
27.0
30.0
Time [min]
A
C
3
1

FIG 3

FIG 2


SRV Wear Scars
height [microns]
0
-5
-10
-15
-20
-25
2000
2500
3000
3500
lateral distance [microns]
2
1

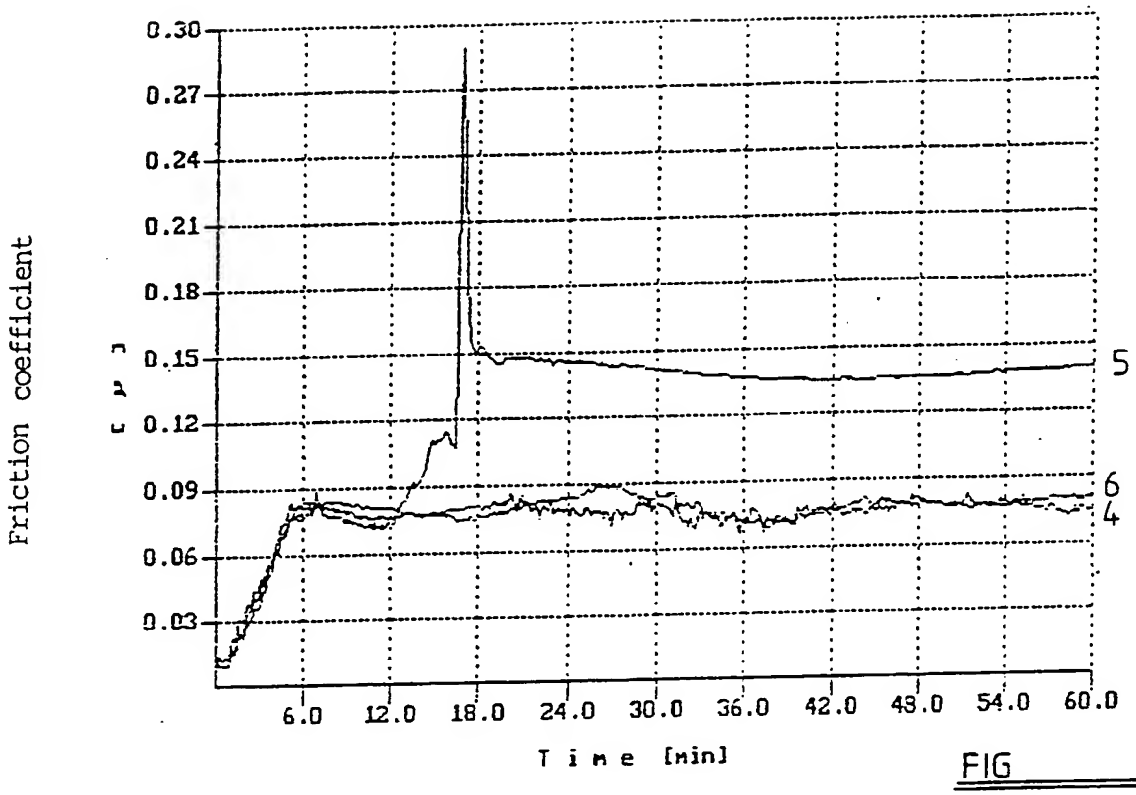


FIG 4

FIG 6

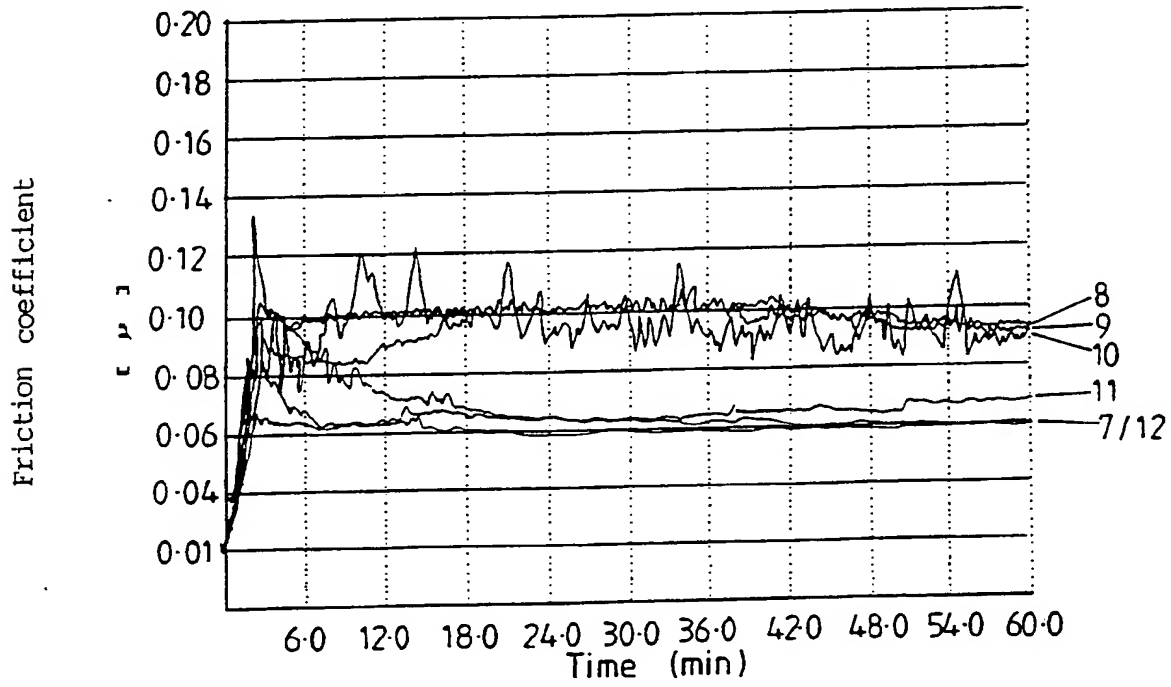
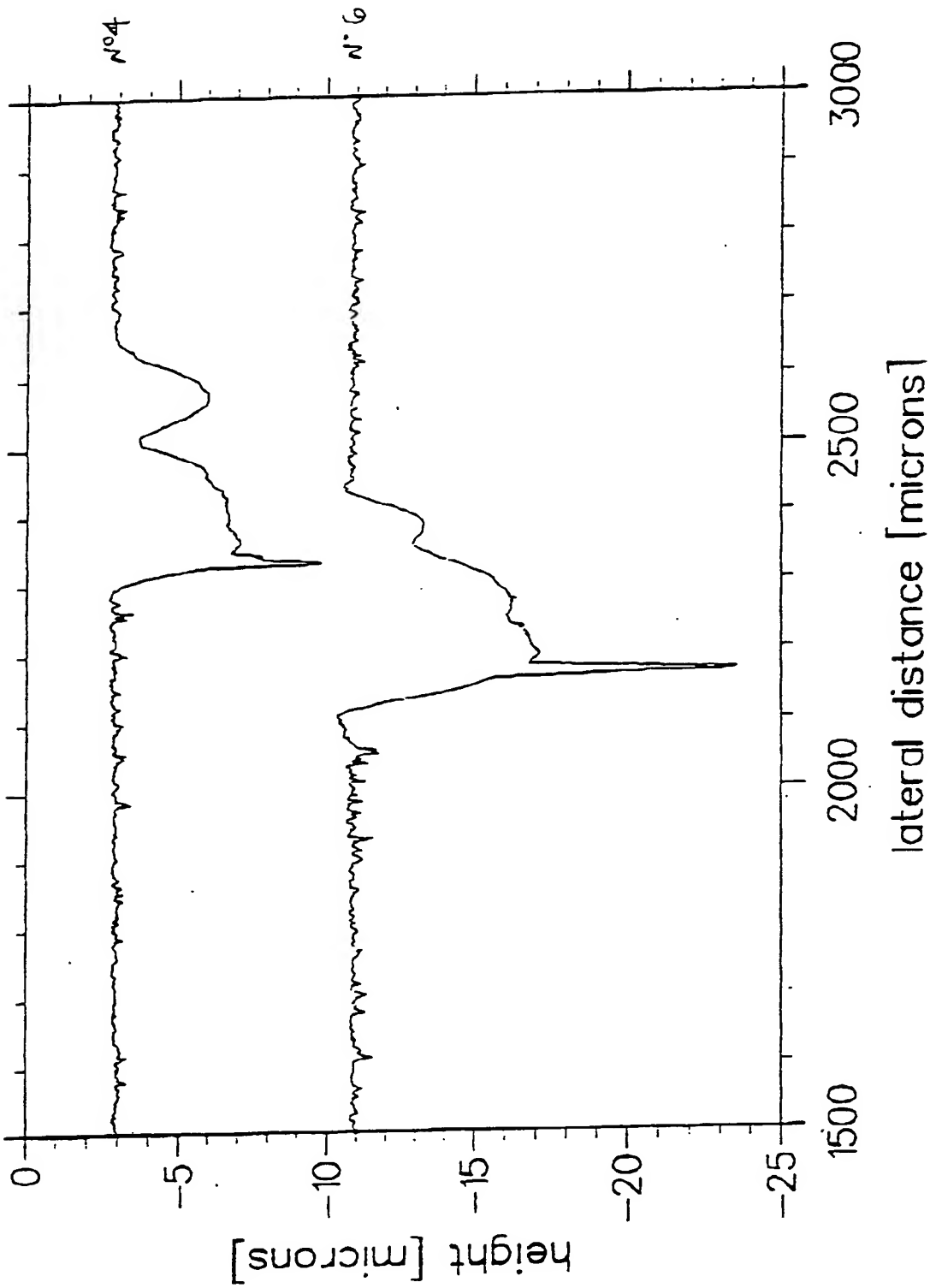


FIG 5



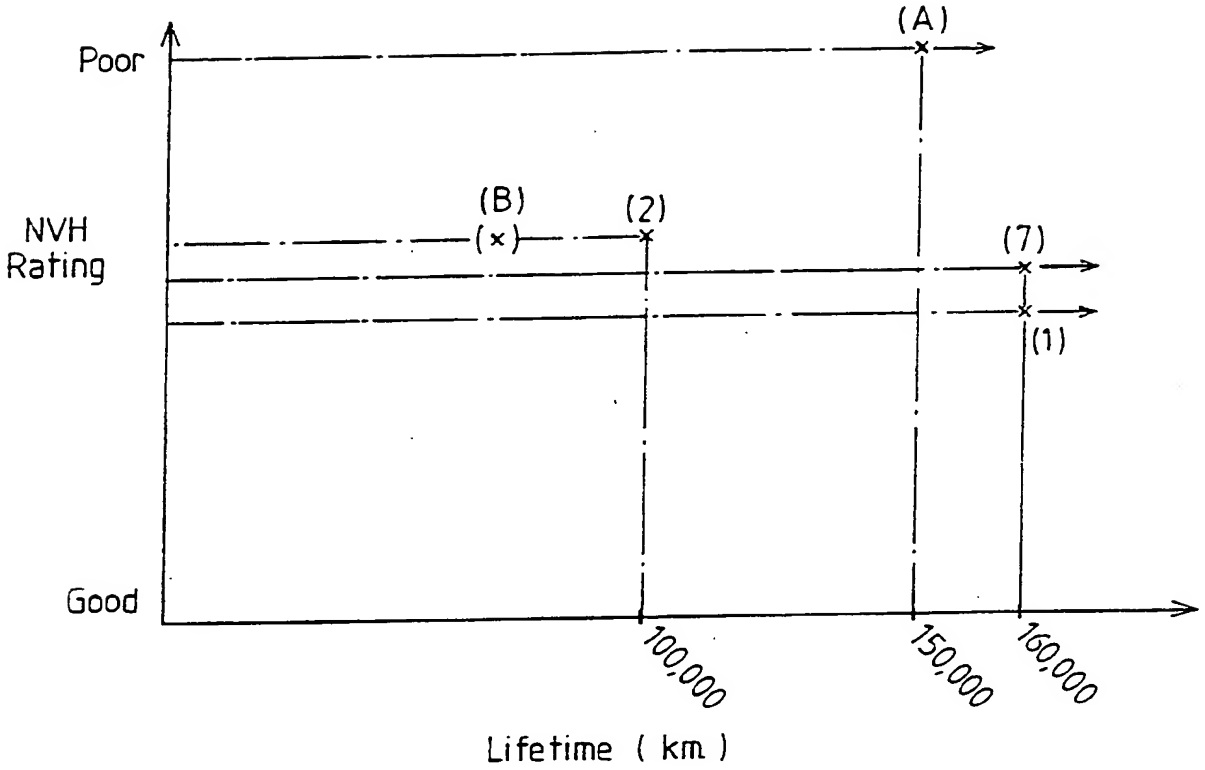

(A)
Poor
(B)
(2)
(7)
NVH
Rating
(1)
Good
100,000
150,000
160,000
Lifetime (km)

FIG 7

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/GB 93/02313

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10M169/06 //C10N10/04,C10N10/12,C10N30/06,C10N40/00,C10N50/10, (C10M169/06,117:02,117:04,117:06,135:02,135:04,135:06,135:36, 135:18,135:18,137:02,137:04,137:10,137:10,137:12,159:18)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 536 308 (R.C.C PEHLER) 20 August 1985 see column 3, line 41 - line 45; table I see abstract ---	1,2,4,5, 9,11-13, 16, 20-22, 26-34
Y	DATABASE WPI Week 8742, Derwent Publications Ltd., London, GB; AN 87-295595 & JP,A,62 207 397 (KYODO YUSHI KK) 11 September 1987 see abstract --- -/--	1,2,4,5, 9,11-13, 16, 20-22, 26-34

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 February 1994	14. 02. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hilgenga, K

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INTERNATIONAL SEARCH REPORT

Intern nal Application No
PCT/GB 93/02313

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 508 115 (NIPPON OIL CO) 14 October 1992 see page 2, line 51 - line 52 see page 17, line 12 - line 45 see page 17, line 57 - page 18, line 2	1-5, 16-20, 22,23, 26-29
A	GB,A,2 255 346 (NTN CORPORATION) 4 November 1992 see page 4, line 16 - line 20 see page 5, line 5 - line 10 see page 5, line 19 - page 6, line 5 see page 6, line 6 - line 11 see page 7, line 2 - line 7	1,2,4,5, 26-34
A	GB,A,2 185 492 (NTN TOYO BEARING) 22 July 1987 see page 2, line 26 - line 63	1-4, 26-34
A	EP,A,0 423 724 (SHIN-ETSU CHEMICAL CO) 24 April 1991 see page 3, line 56 - page 4, line 3 see page 4, line 8 - line 13 see page 4, line 17 - line 22 see page 6, line 1 - line 27	1-3, 20-22,27
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1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/GB 93/02313

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GB-A-2255346	04-11-92	NONE	
GB-A-2185492	22-07-87	DE-A- 3700974	23-07-87
		FR-A,B 2592891	17-07-87
		JP-A- 63046299	27-02-88
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		JP-T- 5504369	08-07-93
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		AU-B- 640857	02-09-93
		AU-A- 1100792	17-12-92
		DE-A- 4204855	08-10-92
		GB-A- 2255103	28-10-92
		US-A- 5207936	04-05-93